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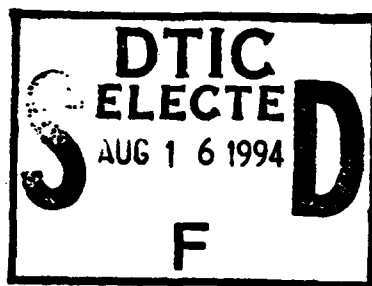


**US-LATIN AMERICAN WORKSHOP
ON MOLECULAR AND
MATERIALS SCIENCES:
THEORETICAL AND
COMPUTATIONAL ASPECTS**

University of Florida

March 10 — 12, 1993

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE August 9, 1994	3. REPORT TYPE AND DATES COVERED Technical Report
4. TITLE AND SUBTITLE 1993 US-Latin American Workshop on Molecular and Materials Sciences: Theoretical and Computational Aspects			5. FUNDING NUMBERS N00014-93-1-0199
6. AUTHOR(S) David A. Micha			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Florida Quantum Theory Project, WM 362 PO Box 118435 Gainesville, FL 32611-8435			8. PERFORMING ORGANIZATION REPORT NUMBER Tech. Rep. No. 1
9. SPONSORING, MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Physics Program 800 North Quincy St Arlington, Va 22217-5000			10. SPONSORING, MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Proceedings of the 1993 US-Latin American Workshop on Molecular and Materials Sciences: Theoretical and Computational Aspects			
12a. DISTRIBUTION/AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited			12b. DISTRIBUTION CODE Unlimited
13. ABSTRACT (Maximum 200 words) This workshop has been made possible by the financial support of the US National Science Foundation, International Programs Division, and by the Office of Naval Research, Physics Division. The early support by the ONR was essential in the beginning stages of the workshop organization; the NSF was very helpful speeding up their reviewing procedure to provide support on a tight schedule. The University of Florida, through its Departments of Chemistry and of Physics, and its Quantum Theory Project, provided help with its staff and with funds at critical times. The workshop attendants from Latin American countries helped this gathering in a very important way, by requesting and obtaining matching funds at their home institutions to travel to the USA. The program of the workshop evolved in response to suggestions from its participants. To begin with, it was decided to organize a short course on molecular and materials sciences based mostly on lectures by the Faculty of the Quantum Theory Project and other US institutions, and to request suggestions on its content from Latin American scientists associated to the University of Florida in past years activities. These suggestions indicated a wish for additional contributions by participants in an informal conference format. The present programs combines the two aims, with a series of half hour overviews followed by long discussions with the participation of the attendants, and with half hour presentations by the attendants on subjects of their disciplines.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

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David A. Micha

Workshop Organizer

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**PROGRAM FOR THE
"US-LATIN AMERICAN WORKSHOP ON MOLECULAR AND MATERIALS
SCIENCES: THEORETICAL AND COMPUTATIONAL ASPECTS"**

WEDNESDAY, March 10.

Afternoon

2:00–2:45 Registration.

2:45–3:00 Opening (Micha, Zerner, Sullivan, Ohm)

3:00–4:00 Lowdin (Overview and discussion).

4:00–4:30 Break

4:30–6:00 Bartlett (Overview and discussion).

Evening

8:00–9:00 Deumens (Overview and discussion).

THURSDAY, March 11.

Morning

8:30–10:00 Micha (Overview and discussion).

10:30–12:00 Monkhorst (Overview and discussion).

Afternoon

1:30–3:00 Ohm (Overview and discussion).

3:30–4:00 Castro

4:00–4:30 Contreras

4:30–5:00 Donnamaria

5:00–5:30 Estiu

5:30–6:00 Fuentealba

6:15-7:15 Social gathering and refreshments

Evening

9:00-9:30 Berrondo

9:30-10:00 Mujica

10:00-10:30 Leite

FRIDAY, March 12

Morning

8:30-10:00 Reynolds (Overview and discussion).

10:30-12:00 Trickey (Overview and discussion).

Afternoon

1:30-3:00 Zerner (Overview and discussion).

3:30-4:00 Nazareno

4:00-4:30 Poulain

4:30-5:00 Recamier

5:00-5:30 Seminario

5:30-6:00 Villaveces

6:00-6:30 Soscun

Evening

8:30-10:00 General discussion.

Titles of the Workshop Presentations

SPEAKER	TITLE
Rodney J. Bartlett UF, USA	Coupled Cluster Methods for Molecular Electronic Structure and Spectra
Manuel Berrondo and Jose Recamier Brigham Young U, USA, and UNAM, Mexico	Complex Eigenvalues in Rotational Predissociation
Sylvio Canuto and Kaline Coutinho U Fed. de Pernambuco, Brazil	Theoretical Studies of the Absorption Spectra of Amorphous Molecular Systems (by title only)
F. M. Fernandez and Eduardo A. Castro UNLa Plata, Argentina	A Factorization Method with Application to Perturbation Theory
Renato R. Contreras U de Chile, Santiago	Ion Solvation from Isoelectronic Processes at its Nucleus
Erik Deumens UF, USA	Computational Facilities for Molecular and Materials Sciences
M. Cristina Donnamaria UNLa Plata, Argentina	Molecular Dynamics of Oligosaccharides
Guillermina Estiu UNLa Plata, Argentina	Semiempirical Quantum Chemical Calculations Applied to a Rational Design of Metal Catalysts
Patricio Fuentealba U de Chile, Santiago	Different Energy Functionals for Modelling the Second-Order Density Matrix
L.M.R. Scolfaro, J.R. Leite et al. U de Sao Paulo, Brazil	Electronic States of n-type δ -Doping in GaAs Heterostructures
Per Olov Lowdin UF, USA	On the Mathematical Foundations of Quantum Theory
David A. Micha UF, USA	Quantum Molecular Dynamics: Fundamental Problems and Some Answers
Hendrik J. Monkhorst UF, USA	Many-Electron Theory for Solids

V. Mujica and M. Garcia Sucre U C de Venezuela and IVIC, Caracas	Scaling and Regional Virial Theorems Beyond the Born-Oppenheimer Approximation
Hugo N. Nazareno and N. H. Shon U de Brasilia, Brazil	Laser Induced Localization and Anomalous Phonon Softening in Superlattices
N. Yngve Ohrn UF, USA	Electron-Nuclear Dynamics: A New Time-dependent Theory for Molecular Processes
Sidonio Castillo Animas and E. Poulain Inst. Mexicano del Petroleo, Mexico City	Activation of C-H Bond by Transition Metals (Cu, Zn, and Cd) and <i>Ab-Initio</i> and Semiempirical Calculations on Catalysis
José Récamier and R. Jauregui Inst. de Fisica, Cuernavaca, Mexico	Iterative Bogoliubov Transformations and Applications
Peter J. Reynolds ONR, USA	Quantum Monte Carlo Methods for Many-body Systems
J.M. Seminario U N de Lima, Peru	Theoretical Chemistry of Energetic Molecules
H. Soscun and P. J. O'Malley U del Zulia, Venezuela and U of Manchester, England	Conformational Preferences for $\text{H}_3\text{SiOHAlH}_3$ Molecules: An Ab Initio Study
Samuel B. Trickey UF, USA	Density Functional Methods for Extended Systems
José Luis Villaveces U N de Colombia, Bogota	On the Mathematical Foundation of Chemical Structure and Reactivity
Michael C. Zerner UF, USA	Some Applications of Electronic Structure Theory

US-LATIN AMERICAN WORKSHOP

Abstracts

University of Florida

March 10 — 12, 1993

BARTLETT RESEARCH GROUP: COUPLED-CLUSTER THEORY AND BEYOND

OUTLINE

I. Coupled-Cluster Theory: What's It All About?

Relationship to CI

Relationship to MBPT

II. Properties: How Do We Do It?

Structure

Vibrational Spectroscopy

Others (moments, polarizabilities, spin densities, relativistic corrections)

III. Excited States and Electronic Spectra

Equation-of-Motion (EOM)-CC Theory

Applications

IV. Photoelectron Spectra

Applications

V. Multi-Reference CC Theory

Fock Space (valence universal) MRCC

Hilbert Space MRCC

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COMPLEX EIGENVALUES IN ROTATIONAL PREDISSOCIATION

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Gamow states are solutions to the Schrödinger equation with a purely outgoing wave boundary condition. For the case of negative real energies, we obtain the bound states of the system. Resonant states correspond to complex eigenvalues, whose imaginary part is the inverse lifetime. Resonant states decay in time, but the time independent part of the wave function diverges at large distances. Numerical integration of the time independent equation is unstable, since the unwanted solution becomes negligible asymptotically and contaminates the numerical solution of the resonant state.

A numerical solution for resonant states can be obtained by integrating different equations in the "inner" and "outer" regions of space. We first propagate the solution starting from a vanishing wave function at the origin. We then integrate inwards the corresponding Riccati equation from the asymptotic region, and finally try to match the logarithmic derivatives at an intermediate point (usually close to the turning point). Use of the (complex) Newton-Raphson formula allows us to iterate the process in order to converge to the correct complex eigenvalue.

Riccati's equation is a nonlinear first order differential equation for the logarithmic derivative of the wave function. It tends to a constant asymptotically, its sign defining the outgoing character of the corresponding wave

function. Inward integration starting from a constant is very stable, even in the complex case.

We applied this method to the resonances in a square well in order to compare with accurately known results. We used a constant step for the two integrations and matched at the discontinuity radius in the potential obtaining excellent results. We used Numerov's method in the inner region, and Runge-Kutta method for the Riccati equation in the outer region.

Rotational predissociation in molecules can be modeled by a Morse potential including the centrifugal barrier. Using the above method, we have computed the bound states as well as the shape resonances due to the centrifugal hump. Sharp resonances are calculated close to the energy threshold and broad resonances are found even above the effective potential maximum!

Theoretical Studies of the Absorption Spectra of Amorphous Molecular Systems

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The theoretical investigation of molecular clusters and molecular systems in condensed phase is a topic of considerable importance and interest [1]. In recent years it has been felt an increased necessity of well-defined theoretical tools for investigating the properties of crystalline and amorphous molecular systems in general [2, 3]. The basic strategy for theoretical calculations of small isolated molecules has been laid down and includes sophisticated schemes both at the *ab initio* and semiempirical levels [4]. For disordered systems, however, the situation is somewhat undefined.

Molecular systems in condensed phase may be conveniently divided in two categories. The first, includes crystalline systems with well defined structural parameters. Given these parameters the crystalline structure can be obtained in an unambiguous and clear way. In the second category one finds the amorphous or disordered systems where the very definition of a structure is not possible. There are in fact many structures equally possible.

Specifically, for the theoretical calculation of the electronic absorption spectra of molecular systems in condensed phase, two basic points have to be considered. First, it is necessary an efficient quantum mechanical theoretical scheme for handling both ground and excited states of a very large system, or a large quantity of similar systems. Typically, from a quantum chemistry point of view, this calls for a semiempirical procedure able to handle, say, 300 to 500 atoms. The second basic point is particularly important for liquids, or disordered systems in general, and it refers to the determination of the structure of the system. A properly defined statistical procedure is necessary in this case [5].

We will present a scheme for the calculation of the visible and UV absorption spectra of molecular systems in amorphous phase [6]. It essentially amounts to a Monte Carlo statistic characterization of the structure followed

by a quantum mechanical INDO-CI [7] calculation of the excited states.

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A FACTORIZATION METHOD WITH APPLICATION TO PERTURBATION THEORY

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Programa QUINOR, Facultad de Ciencias Exactas, UNLP, Calle 47 y
115, C.C. 962, La Plata 1900, Argentina

We present a new implementation of perturbation theory for separable problems which is a blend of two previously proposed factorization methods. The resulting technique offers several advantages with respect to the parent methods and yields the perturbation corrections exactly in terms of the quantum numbers of the unperturbed problem through equations in which the unperturbed eigenfunctions does not appear explicitly. As an example we consider a perturbed Legendre equation and discuss the application of the approach to other problem of physical interest.

**THEORY OF ION SOLVATION FROM ISOELECTRONIC
ENERGY-DENSITY RELATIONSHIPS ***

By

Renato R. Contreras

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Cuántica Aplicada (CMCA), Facultad de Ciencias,
Universidad de Chile, Casilla 653-Santiago
Chile.**

**Keywords : Ion Solvation
Isoelectronic Processes
Density Functional Theory**

(*) Contribution No 7 from CMCA

ABSTRACT.

An approximate theory of the total energy change connected with the embedding of a singly charged positive or negative atomic ion in a polar liquid (ion solvation) is developed. The insertion of the atomic charged system into the polarizable host is modeled through an isoelectronic process at nucleus. In this way, the controversial procedure of selecting appropriate ionic radii, involved in the calculation based on the Born formulation of the insertion energy, is avoided and replaced by a simple isoelectronic processes with a varying nuclear charge. The basic expressions are derived from the variational principle. The resulting expressions are then reformulated within the nuclear transition state (ZTS) model. The reaction field theory expression for the insertion energy is recovered. Finally, a Kohn-Sham like procedure for the calculation of the insertion energy is proposed.

The QTP Computing Facility

Erik Deumens

The QTP Computing Facility is built and maintained by the members of QTP as a group. Resources are acquired as a group and resources obtained individually are usually made available to the entire group on a low priority basis.

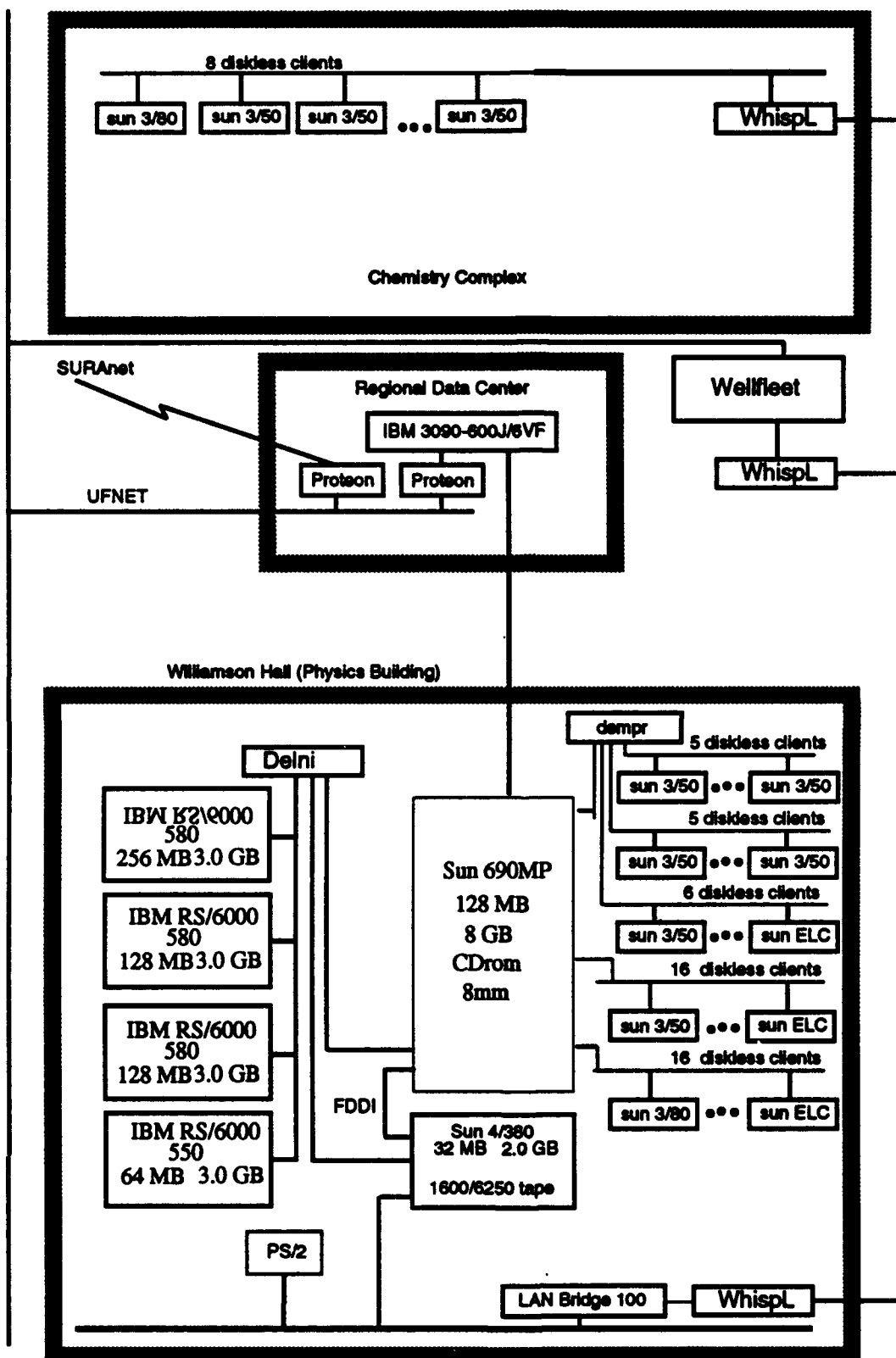
The system consists of a hierarchical structure of 3 environments

1. the work environment provides the user interface with utilities like E-mail, calendar, file manipulation, calculator and primary tools like Emacs editor, desktop publishing with capability to create complex equations with a WYSIWYG editor, high quality graph creation and viewing, source code management, compilation in Fortran 77 and C and interactive debugging;
2. the local production environment provides a batch job system and scratch disks for running small to medium production jobs;
3. the supercomputing environment on campus and in national centers provides a batch job system for very large production jobs.

which are implemented in 4 layers of computers:

1. desktop workstation: 41 Sun 3/50, 3 Sun 3/80 and 12 Sun SPARCstation ELC
2. file servers: 1 Sun SPARCserver 380 and 1 Sun SPARCserver 690MP with 4 processors
3. computer servers: 1 IBM RS/6000-550 and 3 IBM RS/6000-580
4. supercomputers: IBM ES/9000-740 on campus and Cray Y-MP/432 at FSU and other Cray's throughout the U.S.

QTP Computing Network



Revision:19-Apr-1993

1-CONFORMATIONAL BEHAVIOR OF TREHALOSE AS DETERMINED BY MOLECULAR DYNAMIC MODELING

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Trehalose (α -D-glucopyranosyl(1-1) α -D-glucopyranoside) is a disaccharide well known as protector under water stress in plants and as cryoprotector. Although considerable effort has been invested to establish the mechanisms for its action, it is still unclear. Conformational analysis of trehalose have been done by Molecular Dynamics (MD) simulation in vacuum and in aqueous solution (SPC/E water model) using GROMOS package (Biosmos n.v). The results of conformational studies from MD reveal some flexibility of this disaccharide around the glycosidic linkage, which increases moving from the vacuum to the water solution. Some data of MD and Molecular Mechanics (MM2) were already reported.^{2,3} The structure of hydration was studied through radial and angular distribution functions and hydrogen bond statistics. From this analysis in solution the mobility is explained from the lack of internal hydrogen bonds, not only within each monosaccharides but also between them. This study reveals that the presence of trehalose disturbs very slightly the average number and distribution of hydrogen bonds of the water. The almost absence of perturbation of the water lattice cannot be an explanation for the cryoprotection effect.

1.Member of Career of Comision de Investigaciones Cientificas CIC.

2.M.C.Donnamaria, E.I.Howard and J.R. Grigera, Internal Report of ICTP, IC/92/230

3.J.R. Grigera, M.C.Donnamaria and E.I.Howard, Condensed Matter Vol.8 (in press)..

The present study started on Oct. 1990 and belongs to the Project :

"STRUCTURE AND FUNCTION OF BIOMACROMOLECULES" of IFLYSIB

Director: Dr. J. R. Grigera

Members: Dr. J. de Xammar Oro, Dra. M.C. Donnamaria, Lic. E. Cafarena, Dr. J.R. Grigera, Dra. G. Ruderman, Lic. E.I. Howard, Dra. A. Ivancich, Dra. I. G. Mogilner, Lic. E.J.Tolosa. Lic. S. Fasano, Lic. M. Seglie.

This general project works with the relation between structure and function of Biomacromolecules and small molecules of biological relevance. Water, the medium in which life evolves is also considered. As a technique much effort is done in the use of Molecular Dynamics Simulation as a predictive tool of structures in solution. A good success has been obtained in carbohydrates. (Conformational behaviour of Mannitol, sorbitol, α and β -D-glucosa, etc). At present, the group also pursues the problem of prediction of structures related to problems of drug design.

In addition, experimental techniques as dielectric relaxation, electrically induced birefringence and other are also used.

The results have been published in more than 60 papers being reported to national and international Meetings of Biophysics, Physics and Chemistry.

Collaborations:

- * Organic Chemistry Department, University of Groningen, The Netherlands- Dr. S. Galema and Dr. J. B.F.N. Engberts "Study of monosaccharides hydration".
- * IBMC, Estrasburgo- Dr. A. Podjardy . "Study of Biomacomolecules using X ray Diffraction and MD".
- * PROFIMO-University National La Plata:-Dr. J. Maranon- "Dynamic Simulation of Adenine Conformational Behaviour"

Resources.

This project is supported by CONICET, CICBA and Fundacion Antorchas. Molecular Dynamics Simulation was done using the GROMOS package (Biomos n.v., Groningen-Zurich) running in an IBM RS6000 32H. Results were analysed in a VAX 11/750, a Micro Vax Work Station, and in a 486 personal computer. The Institute also deals with a complete laboratory for doing measurements of dielectric properties.

SEMIEMPIRICAL QUANTUM CHEMICAL CALCULATIONS APPLIED TO
A RATIONAL DESIGN OF METAL CATALYSTS.

Guillermina Lucia Estiú.

Proyecto Quinor. Facultad de Ciencias Exactas. Universidad Nacional de
La Plata. Casilla de Correo 982- 1900- La Plata - ARGENTINA-

Because of the extensive technological applications of metal systems in several areas of catalysis, electrochemistry and micro electronics, a large effort has been focused to understand the chemical and physical properties of metal bonds.

Research in metallic systems has reached nowadays a level where their properties are actually design on the basis of theoretical considerations. This non empirical design of industrially important metallic systems implies a challenge to the modern scientist, responsible of answering several questions that have remained opened after the experimental evidence accumulated during the last 50 years. Concern is mainly related to the nature of the interactions, either metallic-non metallic (adsorption phenomena) or homo or heteronuclear bimetallic (cohesion, adhesion). The nature of the interaction is related, on the other hand, to the local environment of the bond, which will be different for surfaces and small metal particles, homogeneous or bimetallic systems, gas phase or electrochemical media.

The large number of conditions that must be defined to fully specify a system allows one to rationalize their influence by means of a systematic analysis of the change of its behavior in response to changes in the environment. This rationalization is the basis for a non empirical design of a catalyst, and is based, on the other hand, on the knowledge of the related molecular orbital interactions.

Quantum chemical calculations are capable, nowadays, of modeling 2D periodic metal surfaces, fully optimize the structure of small metal particles and analyze the influence of different internal and/or external perturbations, defined by included foreign atoms, co adsorbed species or even external potentials, being the two latter

particularly important for electrocatalytic processes. The explanation, at a molecular orbital level, of the different effects, is the answer on which basis the phenomena can be understood and the importance of the different factors can be quantified.

The general properties of a metal center depends, in the most general definition, on three factors: i) the metal itself, ii) the type of species bonded to the metal, and iii) the geometrical structure of the site. While the second factor takes into account the influence of the environment, the third one differentiates between extended surfaces and small particles in supported catalysts. The importance of the d orbitals in the determination of the catalytic activity has oriented most of the research to the study of compounds containing atoms of the 2nd and 3rd transition metal rows, where the large number of orbitals defining open shell structures are a difficult task for SCF calculations and reminds the theoretical chemist that a lot of work needs to be done on an accurate parameterization of the semiempirical techniques.

The analysis, at a molecular orbital level, of the influence of the geometry, as well as internal and/or external perturbations on the reactivity of a metal structure towards a given reaction, is the first step towards a rational design of mono and bimetallic catalysts. Because of its importance in catalysis and the sensitivity of its spectroscopic features to the changes in the local environment, the adsorption and electrooxidation of CO is a particularly suitable test reaction. It has been analyzed, at the SCF level, in the interaction with Rh structures, giving an explanation to the larger reactivity of highly dispersed supported catalysts [1-3]. There is still a lot to learn about this system. Present research is oriented to understand the influence of internal and external perturbations on the reactivity of Rh based catalysts as well as on the nature of the intermediates involved in the reaction mechanisms.

1- G.L. Estiú and M.C. Zerner, Int. J. Quant. Chem.: Quant. Chem Symp. 26 (1992) 587.

2,3- G.L. Estiú and M.C. Zerner, manuscripts in preparation.

ABSTRACT

Different Energy Functionals from modelling the second-order density matrix

In this communication starting with a general Ansatz for the diagonal elements of the reduced second-order density matrix different energy functionals have been obtained. An interparticle coordinate expansion followed by an approximate Gaussian resummation of the second-order, and first-order density matrix, which has provided to be a powerful technique /1-3/, has been used.

Model functionals for the total electron-electron energy, the exchange-correlation, the exchange and the correlation energy will be presented.

The electron-electron repulsion energy functional is a slight improvement on an Ansatz given by Parr /4/, and the results compare very well with the Hartree-Fock values for the noble gas atoms.

The exchange-correlation energy functional has been obtained using the cusp and normalization condition of the second-order density matrix. Results for several atoms and ions have shown the feasibility of the approach /5/.

The exchange energy functional comes from modelling the Hartree-Fock second-order density matrix. Only the matrix elements representing an electron pair of like spin have been considered. /6/. It represents a complement to models based on the exchange hole.

The correlation energy functional has been obtained from a gradient expansion of the correlation factor. It has been possible to recover the empirical functional

published by Levy /7/, but with different parameter values.

The functionals presented in this communication share some important features. Since the normalization condition of the second-order density matrix has been in all cases satisfied they depend on the number of electrons. They do not have more than one empirical parameter to be adjusted, and the homogeneous-electron gas approximation has not been used.

At the end, problems and possible extensions will be discussed.

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On the Mathematical Foundation of Quantum Theory.

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It is hoped that some day one will be able to formulate the mathematical foundation of quantum theory including the theory of the interaction with electromagnetic fields and the special theory of relativity as a deductive theory in a completely logical way. For this purpose one has to go over the fundamental assumptions - the axioms - once more and also to study the structure of the deductive theories in general. - In the 19th century, it was realized that the *axioms* are not self-evident theorems, which do not require any proof, but building stones of a theory introduced by choice, which should be non-contradictory and non-redundant. A deductive theory contains further as a rule some fundamental quantities, which are not defined by the axioms, and are hence often referred to as *undefined quantities* without immediate content. In the last century, the mathematicians started formulating abstract theories which were as content-less as possible, as e.g. abstract group theory. If one defined the fundamental quantities in a specific way, one obtains a *realization* or model of the abstract theory, and an abstract theory has often many different realizations.

When modern quantum theory was developed around 1925, an important question was how one should interpret the position x and momentum p of a particle in the new theory. Dirac did not define these quantities, he called them *q-numbers* which satisfy the commutation relation $px - xp = h/2\pi i$, Schrödinger defined them as *operators* which form the foundation of wave mechanics, whereas Heisenberg, Born and Jordan interpreted them as *matrices* leading to a matrix mechanics.

In 1931, Goedel proved his famous *insufficiency theorem* saying that, in a deductive theory based on a finite number of axioms, there are well-formulated theorems which cannot be proven to be true or false within the system. In the 1960's Cohen pointed out that, if there are theorems which are true in one realization but false in another, they must necessarily be goedelian in the abstract theory. This means also that, in the abstract theory, there are goedelian branching points corresponding to the various realizations. The various types of non-euclidian geometries form a good example of this type of behavior.

In discussing the axioms of modern quantum theory, we will following v. Neumann [1] consider an ensemble of physical systems prepared in exactly the same way. It may be convenient to start from the assumption that every physical observable \mathcal{F} corresponds to a linear operator F (ax.1) defined on a separable Banach space $B = \{x\}$ having a well-defined norm $\|x\|$. The separability of the space indicates that there exists a basis $\mathcal{X} = \{X_1, X_2, X_3, \dots\}$ which spans the space, i.e. every element x may be expanded in the form $x = \sum_k X_k a_k = \mathcal{X} a$. For an operator T , one has $T X_i = \sum_k X_k T_{ki}$, which defines the matrix representation $T = \{T_{ki}\}$ of the operator. In order to describe the operator space $\{T\}$, it is convenient to introduce the operators P_{ki} which are defined through the relations $P_{ki} X_m = \delta_{km} X_i$. Since one easily proves the relation $T = \sum_k P_{ki} T_{ki}$, it is evident that the operators P_{ki} span the operator space $\{T\}$; they are hence often referred to as the fundamental units of this space.

In the experiments, one measures the average value $\bar{\mathcal{F}}$ of \mathcal{F} and assumes that, in the theory, it corresponds to an *expectation value* $\langle F \rangle$ of the operator F . One assumes further that $\langle T \rangle$ is a *linear functional* of the operator T with the property $\langle I \rangle = 1$ (ax.2). Using the expansion of T in terms of the fundamental units, one obtains directly $\langle T \rangle = \sum_k \langle P_{ki} \rangle T_{ki}$, where the quantities $\langle P_{ki} \rangle = \Gamma_{ki}$ must be characteristic for the ensemble under consideration. The operator $\Gamma = \sum_k \Gamma_{ki} P_{ki}$ defines the ensemble or *system operator*, the kernel of which is known as the density matrix ρ . Since all expectation values may now be written in the form $\langle T \rangle = \text{Tr } \Gamma T$, this approach is sometimes referred to as the *trace algebra* [2]. If all the physical results of the theory are expressible in terms of expectation values, one hence needs only a Banach space as the carrier space for the operators, and one does not have to worry about a metric. Once this is clear, it may be convenient to introduce the space which has the simplest metric: the *Hilbert space*, since it has been studied mathematically in great detail. It has a binary product of the form $\langle x|y \rangle$ with a non-negative norm $\|x\|^2 = \langle x|x \rangle \geq 0$, and the adjoint operators T' defined through the relation $\langle T'x|y \rangle = \langle x|Ty \rangle$.

Since $\bar{\mathcal{F}}$ corresponds to $\langle F \rangle$, it is natural to assume that the expectation value $\langle F \rangle$ is real, i.e. $\langle F \rangle = \langle F \rangle^*$, (ax.3). Since one has $\text{Tr } T' = (\text{Tr } T)^*$, one finds easily the sufficient condition $F' = GFG^{-1}$ and $\Gamma' = G\Gamma G^{-1}$. In the case when one follows Schrödinger's recipe and chooses the physical operators as self-adjoint with respect to the L^2 Hilbert space, one obtains $F' = F$ and $\Gamma' = \Gamma$. This implies that all the eigenvalues n_k of the system operator are *real*.

Next we observe that for the experimental width $\Delta\mathcal{F}$ one has always $(\Delta\mathcal{F})^2 = \bar{\mathcal{F}}^2 - (\bar{\mathcal{F}})^2 \geq 0$, and $\Delta\mathcal{F} = 0$ only for a sharp measurement,

and it is hence natural to assume that, for the theoretical width ΔF , one has also $(\Delta F)^2 = F^2 - (\bar{F})^2 \geq 0$, (ax.4). It is then easily shown that the eigenvalues n_k can never be non-negative, $n_k \geq 0$. Since $\langle 1 \rangle = \text{Tr } \Gamma = 1$, one finds finally that the system operator Γ has the fundamental properties

$$\Gamma^\dagger = \Gamma, \quad \Gamma \geq 0, \quad \text{Tr } \Gamma = 1.$$

We note further that the eigenvalue properties $n_k \geq 0$ and $\sum_k n_k = 1$ make a *probability* interpretation of the ensemble theory possible.

It is easily shown that the set $\{\Gamma\}$ of all system operators is a *convex set* with exterior points having the property $\Gamma^2 = \Gamma$. Since they are one-dimensional projectors of the form $\Gamma = |\Psi\rangle\langle\Psi|/\langle\Psi|\Psi\rangle$, they correspond to the case of pure quantum mechanics, whereas the interior points correspond to general quantum theory dealing also with canonical ensembles, dissipative systems, etc. Of essential interest are the convex functionals formed on this set, and we note that the only additive functional is proportional to $-\text{Tr } \Gamma \log \Gamma$ and is called the *negentropy*.

If one assumes that the carrier space undergoes a time evolution of the form $\Psi(t) = S \Psi(0)$ and further that the mapping $\phi(t) = \Gamma(t) \Psi(t)$ is invariant for all t (ax.5), then the system operator undergoes a similarity transformation $\Gamma(t) = S \Gamma(0) S^{-1}$ with time. Taking the time derivative of these relations, and introducing the notation $M = (dS/dt)S^{-1} = -S(dS^{-1}/dt)$ one easily derives the analogues of the Schrödinger equation and the Liouville equation

$$d\Psi/dt = M\Psi, \quad d\Gamma/dt = M\Gamma - \Gamma M,$$

with the Hamiltonian $H = (-\hbar/2\pi i) M$. It is evident that the similarity transformation gives rise to some of the commutation relations characteristic for quantum theory. For more details the reader is referred elsewhere [2].

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QUANTUM MOLECULAR DYNAMICS

Fundamental Problems and Some Answers

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ABSTRACT

A full quantal treatment of all electrons and nuclei in a molecular system presents fundamental theoretical problems as well as practical computational ones. This overview deals with some possible answers to the theoretical problems, and presents results of computational studies for selected molecular and materials systems. Subjects to be presented include:

- Electronic representations and the time-evolution of molecular states.[1]
- The coupling of degrees of freedom with short (electronic) and long (nuclear) time scales.[2]
- State-to-state transitions and the requirements for time-reversal invariance.[3]
- The limit of short wavelengths (eikonal limit) for semiclassical degrees of freedom.[4]
- Localized electronic rearrangement in extended systems.[5]

Some of our results will be presented for slow atom-atom collisions, and for slow atom - solid surface collisions involving electron transfer. The relevance of recently developed concepts and computational techniques will be discussed in connection with intermolecular and intramolecular electron transfer.

If time allows it, an overview will be presented of collisional time-correlation functions, their relation to energy transfer and photodissociation in extended systems, and how to calculate them in electronically adiabatic phenomena.[6]

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ABSTRACT

Many-electron Theory for Solids

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When considering the calculation of electronic properties of solids with accuracies higher and more systematic than the Local Density Approximation(LDA) great care is needed to choose the hierarchy of many-body corrections. In particular, the traditional approaches of quantum chemistry, starting from Hartree-Fock wavefunctions and energies followed by Configuration Interaction(CI), Many-Body Perturbation Theories(MBPT), etc. are totally inadequate. Conditional convergencies arise from Madelung-like summation steps in integral evaluations; infinities in finite-order MBPT; and pathologies in densities of states and bandwidths and gaps at the HF level and even beyond prohibit the extraction of physically well-behaved quantities. In direct-space representation calculations(involving direct lattice sums) these problems are often hidden from sight, and only show as an unusual behavior in such quantities. I advocate that all extended, periodic system calculations should be conducted in momentum representation, and that Green's function techniques should be used to give a balanced treatment of exchange and correlation corrections beyond a Hartree-level zeroth order band calculation with a mixed atomic-orbital/plane-wave basis set. Fast Fourier Transform techniques can be used advantageously, and very involved unit cells can be handled. Relationship to LDA can be most easily discerned and exploited. However, the manifest ability to systematically go beyond LDA is the most powerful feature of the approach.

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SCALING AND REGIONAL VIRIAL THEOREMS BEYOND BORN-OPPENHEIMER APPROXIMATION

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Abstract

Recent work on applications of real scaling in molecules which is not restricted to the Born-Oppenheimer approximation is presented. The basic concept is that of regional energy, which is associated with either particles or coordinates, and from where a variational calculation allows the construction of partitions in three-dimensional space where the virial theorem is obeyed. It is shown that there exists a large variety of these so-called virial surfaces, and that they depend on the nature of the quantum particles or collective coordinates chosen.

We present the formalism and examined general cases when the nuclear motion may introduce important modifications of the surfaces corresponding to the fixed nuclei model. Applications to very simple molecular cases are considered. The latter are mainly performed as a way of comparing our results with those obtained by Bader and collaborators within a scheme that partitions real space based on the properties of the electronic density.

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LASER INDUCED LOCALIZATION AND ANOMALOUS PHONON SOFTENING IN SUPERLATTICES

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Since the experiment done by A Kueny et al [1] interest arised on the problem of anomalous velocity of acoustic waves in superlattices (SL). This anomaly is related with changes in the electrical resistivity of the material. The object of the present work is to present a first principle calculation that shows that this phenomenom is associated with the induced localization of electrons by a laser field [2] - [5]. It is known that the bandwidth of a SL can be tunned almost at will by the application of an ac electric field along the growth direction of the structure. In fact if Δ is the miniband width for the free field case by applying a field of intensity F and frequency ω we get a renormalized bandwidth given by $\Delta J_0(eFd/\omega)$.

In this way it is possible to obtain very narrow bandwidths 1 meV. We present here a theoretical model based in the Kubo formalism that could well explain the localization of acoustic waves as a result of the induced collapse of minibands brought about by the application of an ac electric field.

Since the prionnering work by Anderson [6] much effort was devoted to the study of localization in random media mainly dealing with electronic processes. A more recent study by John [7] brought about the problem of localization of acoustic classical waves in a random medium.

In the work of ref. [1] it was reported a strong phonon softening on Cu/Nb SL i.e. the presence of a clear dip in the wave velocity which in turn is associated to a drastic change in the electric conductivity of the sample. More recently Graham et al [8] reported clear evidence of localization of acoustic waves by observing strong atenuation peaks as well as renormalization of sound velocity.

In summary, we have solved the quantum Liouville equation for the case of a superlattice excited by an acoustic wave in the presence of a laser field. In doing so we have obtained a generalized Kubo formula. Our calculation predict a strong sound velocity renormalization and intensive absorption peaks whenever the dynamic localization conditions are fulfilled.

On experiments done in SL [1] it was found a very strong renormalization (15 %) of sound velocity which could well be explained by the present model.

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Electron Nuclear Dynamics; A New Time-Dependent Theory for Molecular Processes.

by
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The recently developed and implemented END (Electron Nuclear Dynamics) method is described and results presented for its application to the calculation of elastic and charge transfer cross sections for prototypical ion-atom and ion-molecule collisions. In this method the equations of motion are obtained using the time-dependent variational principle (TDVP) with a group theoretical coherent state parametrization of the wavefunction. This fully dynamical method describes the molecular processes without the use of potential energy surfaces and relies on the instantaneous forces between all nuclei and electrons, i.e. does not invoke the Born-Oppenheimer approximation.

Current implementations use a single determinantal description for the electrons and classical nuclei. Results for protons colliding with hydrogen atoms, helium atoms, and hydrogen molecules show excellent agreement with experimental results, but differ in some cases at lower collision energies with the results from close-coupling calculations.

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Iterative Bogoliubov Transformations: Applications

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Abstract

We have applied a sequence of generalized Bogoliubov transformations to the creation and annihilation operators of an anharmonic oscillator in order to obtain a new set of boson operators in terms of which the anharmonic potential can be approximated by its diagonal part for the evaluation of the energy eigenvalues. We also made a perturbative calculation and a variational one and have found that the number of basis functions in order to reach convergence is smaller when one applies the transformations.¹ Finally we showed how the transformations can be used for the description of the dynamics of wave-packets in anharmonic potentials.²

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Quantum Monte Carlo Methods for Many Body Systems

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I briefly introduce the Monte Carlo concept and illustrate it with some simple examples. Starting with the uniform distribution I will show how general distributions can be generated. Detailed balance and methods of satisfying it will be discussed. This will lead naturally to variational Monte Carlo (VMC), which is a method of evaluating quantum expectation values given a trial wave function. Following this the discussion will turn to the true quantum problem and its stochastic solution via the quantum Monte Carlo (QMC) approach. This solves the many-body Schrodinger equation in an in-principle exact fashion, though it is statistical in nature. Approximations which tend to be made can be eliminated, and are not related to the ability of the method to treat electron correlation. For pedagogical reasons, the QMC method will be illustrated via the short-time approximation and the resulting diffusion QMC method.

Following this, I discuss some of the shortcomings of QMC, including the sign problem and the large-Z problem, and methods that we have proposed to help overcome them. The fixed node approximation for the sign problem will be discussed. The most obvious methods for treating the large-Z problem include use of pseudopotentials, hybrid Monte Carlo approaches, and acceleration algorithms. A Metropolis-GFMC hybrid allows a separation of the relevant core and valence time scales, and has sped up simulations by over 3 orders of magnitude. A distinctly different point of view is embodied in acceleration algorithms, which made their appearance independently in simulations of quantum chromodynamics on lattices and in statistical mechanics simulations of spin systems. The acceleration approach as implemented for QMC modifies the dynamics in Langevin-based simulations in such a way that the steady-state distribution is unchanged, but may be sampled more quickly. Problems remain with this approach.

Finally, I will summarize some recent work on extending QMC to treating expectation values of quantities other than energies, and in treating multiple states, as in the calculation of transition dipole moments. A number of algorithms will be described briefly. One employs a single QMC random walk, while another involves a VMC random walk with auxiliary QMC "side walks." A tagging algorithm used for efficiently tracking descendants of a walker will be described for each approach. For the single-walk algorithm it is found that carrying weights together with branching significantly improves efficiency. Algorithms for computing transition dipole moments will also be discussed. The simple, but approximate, second-order or "extrapolated" estimator will be demonstrated also, and compared with the exact algorithms. Results will be presented for simple test systems such as the oscillator strength and excited-state lifetime for a Li atom transition, and will be compared with experiment. Agreement is found to be phenomenal.

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ELECTRONIC STATES OF n-TYPE δ -DOPING IN GaAs HETEROSTRUCTURES

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Key words: Heterostructures, 2D electron gas, δ -doping

The electronic properties of silicon δ -doped GaAs heterostructures grown in our laboratory by Molecular Beam Epitaxy (MBE) are investigated by both, theoretical and experimental methods. Magneto-transport and photoluminescence measurements are performed to study Si δ -doped GaAs quantum wells and periodically Si δ -doped GaAs layers. With these independent techniques, both, the electronic structure and the optical transitions involving the quantum confined states are probed. Self-consistent one-electron state calculations within the framework of the effective mass approximation, are carried out to determine potential profiles, electronic subband energies and occupations, charge densities and miniband dispersions. Exchange-correlation effects, according to the local density approximation, and the possibility of silicon diffusion out of the doped plane are also taken into account in the calculations. A systematic study of the carriers confinement due to the presence of the GaAlAs barriers in the δ -doped quantum wells is performed, as a function of well width and dopant concentration. Similar analysis are done for the periodically Si δ -doped GaAs layers, in which the doping period, donor concentration and diffusion are varied. The enhancement of the confinement in these structures is clearly observed from the increasing of the Fermi energy as indicated in the photoluminescence spectra.^{1,2}

The effect of band gap renormalization, taken into account through its dependence with carrier density, has shown to be extremely important in the description of the quantum-confined optical transitions in these systems.

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***Conformational Preferences for $H_3SiOHAlH_3$ Molecules:
An *ab initio* Study***

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ABSTRACT

In the present work, we report a conformational analysis of the rotational isomers of $H_3SiOHAlH_3$ (a cluster model for bridged hydroxyl groups in zeolites). It is demonstrated, by *ab initio* molecular orbital methods at the Hartree Fock and Post Hartree Fock levels, that previous investigations have used a first order transition state as model of zeolite framework. We report the true minimum energy for $H_3SiOHAlH_3$. Also, implications for the structure and location of bridged hydroxyl groups in zeolites are discussed.

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DENSITY FUNCTIONAL METHODS for EXTENDED SYSTEMS

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After nearly 30 years of development, density functional theory (dft) is the standard by which all other electronic structure treatments of large systems are measured. Its range of successes is so broad that the title is unrealistic; we can only illustrate a few of the more interesting recent developments and applications.

The presentation is organized in four segments: (1) a review of the basics of Hohenberg-Kohn-Sham theory from the modern perspective (constrained search) followed by a reprise of what is well understood and not well understood about the theory and a list of useful references; (2) a quick summary of the algorithms in FILMS [J.C. Boettger and S.B.T., J Phys. F 16, 693 (1986); J Phys. Condens. Matt. 1, 4323 (1989)], an example of a modern all-electron, full-potential code for a highly anisotropic system, namely an unsupported, ordered, ultra-thin film ($\nu = 1, 2, 3 \dots$ atomic planes); (3) results from FILMS calculations including interplanar expansion at a Be surface [J.C. Boettger and S.B.T., Phys. Rev. B 32, 1356 (1985); Davis et al., Phys. Rev. Lett. 68, 2632 (1992)], quantum size effects in Li ν -layers [J.C. Boettger and S.B.T., Phys. Rev. B 45, 1363 (1992)], and strain-dependent critical points in the magnetization of an Fe 1-layer [J.C. Boettger, Phys. Rev. B 47, 1138 (1993)]; (4) recent work on generalized gradient approximations (as a step beyond the local spin density approximation) which has the so-far ironic outcome that those approximations seem to be a major step forward for finite systems but not for extended ones [J. Perdew, Physica B 172, 1 (1991); Perdew et al. Phys. Rev. B 46, 6671 (1992); Garcia et al., Phys. Rev. B 46, 9829 (1992)].

Work supported in part by U.S. Army Office of Research

UNIVERSIDAD NACIONAL DE COLOMBIA
GRUPO DE QUIMICA TEORICA

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ON THE MATHEMATICAL FOUNDATIONS OF CHEMICAL STRUCTURE AND
REACTIVITY

We are interested in arriving to a precise concept of chemical structure. To do that, we begin by remembering that since the introduction of this idea by the mid-XIX century, it was recognized that chemical structure should be a concept structurally stable for which the important things are neighbourhood relationships and symmetry. Actually, chemical graphs arose from the work of Kekulé and Butlerow around these ideas. A second line of thought, coming from LeBel and Van t'Hoff, interpreted chemical structure as a geometrical concept. This idea was strengthened between 1930 and 1980 with results from quantum-chemical optimizations and X-ray diffractions. Recently, the need for a revision of these thoughts has been felt, mainly because reducing a chemical structure to a point in ^{3N}R violates Heisenberg principle.

Several essays to construct a topological definition of chemical structure have been proposed during the last decade. These definitions are not equivalent in principle, as Mezey conjectured. However, we have found the conditions to establish an abstract topological definition of a chemical structure, from which all others may be deduced as particular realizations. All topological spaces fulfilling this condition may be shown to be homeomorphic and then equivalent in a large topological sense. The quotient of any of these topological spaces by its corresponding equivalence relation gives exactly the same quotient space, which is, thus, independent of any choice of equivalence property.

A chemical structure may then be defined as the category whose objects are:

1) the configuration space mR , with the topology generated by any particular equivalence relation: $G=\{^mR, T_c\}$; 2) Q , the quotient space; 3) the relationship giving the quotient space: $q: G \rightarrow Q$.

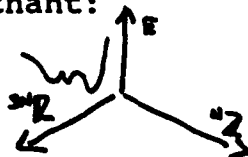
The morphisms of this category, (which are strictly isomorphisms), relate all these possible triplets:

$$u: (G, q, Q) \rightarrow (G', q', Q)$$

This suggests a fibered space structure. To take advantage of that fact, it is convenient to define a local metric in G . The introduction of which allows us to recuperate the differentiability properties of E and to distinguish between points corresponding to different stable chemical structures.

A second problem, once defined the chemical structure is that of finding a chemical reactivity definition in the framework of the theory of categories. A regular chemical reaction may be defined by a set-theoretical neighbourhood relationship. The question is under what conditions a morphism keeps invariant the neighbourhoodness. This happens whenever it is an uniformly continuous isomorphism, giving us the mathematical condition for an invariant definition of chemical reaction mechanism. To go further into this question requires probably a study of the dynamics of the system.

As the Hamiltonian of a molecule depends on the spatial coordinates of electrons and nuclei, as well as on the nuclear charges, to consider the hyperpotential surface as dependent only on R is a partial view, corresponding to its projection onto one of the hyperfaces of the positive orthant:



We have extended prior results in $E(Z)$, making explicit the dependence of the energy upon the nuclear repulsions, obtaining some interesting relationships. In particular, we have probed, for total Z up to 3 -and it seems that the proof may be generalized-, that the total energy of any molecule lies between the energy of the united atom and that of a cluster of Z hydrogen atoms with the same geometry, giving thus lower and upper bounds, respectively, for this energy.

Some Applications of Electronic Structure Theory

Michael C. Zerner

Abstract:

In this talk three examples are developed of using electronic structure theories to answer specific problems that have interested me and the members of my group.

In the first example we consider large molecular systems and clusters in which the number of possible electronic states makes the self-consistent-field (SCF) procedure uncertain. In the case, for example, of Rh_{51} (a piece of the (111) surface) there are some 10^{19} states that are expected to lie close in energy. The SCF procedure will not give useful results without modification; indeed the SCF procedure will not converge.

Open-shell methods are reviewed, and a new restricted open-shell Hartree Fock procedure outlined (ROHF). A method of averaging over all possible states that arise from N electrons in m orbitals is derived and tested on small metal clusters and a seven coordinated Fe(II) compound with well characterized properties. This configuration averaged Hartree-Fock (CAHF) procedure is followed by a simple valence bond projection demonstrating the single SCF calculation with projection yields competitive results to separate ROHF calculations on the states of different multiplicities, but is computationally far less demanding. Indeed, the CAHF procedure effectively converges and always yields orbitals of use for further post Hartree-Fock procedures.^[1-4]

As a second example a review of methods used to calculate excited states is made. Configuration interaction methods and ΔSCF models are useful, but, although frequencies are often well reproduced, oscillator strengths are not. A review is made of the RPA method and its implementation into the INDO/CI-spectroscopic

model. This model focuses in some sense on the accurate calculation of transition moments, and several examples are shown where results from CI and RPA calculations yield similar transition energies, but quite different oscillator strengths. The spectrum of free base porphyrin is reviewed, and it is suggested that the original interpretation of this spectrum is correct, not the more recent re-interpretation that has resulted from CI calculations.^[5-8]

The third example given concerns the initial photochemical event in photosynthesis. Light is absorbed and leads to a separation of charge that eventually supplies the energy required to break the strong bonds of carbon dioxide, the first step in carbon atom "fixation". SCF-CI calculations are reported on bacterio-chlorophyll, bacterio-chlorophyll dimers, and finally on the reaction center itself, a system containing six chlorophyll molecules with over 500 atoms and 1500 electrons. These calculations suggest how the absorption takes place, and how this initial event leads to the observed charge separation. Arguments are made for the path the electron follows in this transfer - a path that has led to some controversy in the past.^[9-10]

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